

# Unexpected sulfur isotope fractionation associated with pyrite oxidation by hydrogen peroxide at temperatures from 4 to 150°C

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Radiolytic cleavage of water produces a mixture of strong oxidants (including H<sub>2</sub>O<sub>2</sub>) and reductants if the products do not quickly recombine as water molecules. Radiolysis in subsurface environments can produce gradients of both electron acceptors and electron donors that are potential sources of energy for microbiological communities. Radiolytic generation of oxidized sulfur species in the absence of an oxygen-rich atmosphere is critical to understanding the sulfur cycle during the Archaean on Earth and during evolution of other potentially habitable bodies such as Mars and Europa.

In order to investigate potential isotopic effects associated with the radiolytic oxidation of pyrite we have performed a series of sealed-tube experiments, done at concentrations of H<sub>2</sub>O<sub>2</sub> from 0.2 to 0.02mM and at temperatures from 4 to 150°C. Water used in these experiments was de-oxygenated to minimize competing reactions with O<sub>2</sub>.

In initial experiments, the dominant products were hydrated iron sulfates and elemental sulfur. Dissolved sulfate and elemental sulfur were enriched in <sup>34</sup>S compared with initial pyrite to an unexpected extent. No gaseous, aqueous, or solid sulfur species were recovered with compensating <sup>34</sup>S depletion. The degree of <sup>34</sup>S enrichment appears to reflect valence, with sulfates enriched by 0.5 to 1 per mil and elemental sulfur enriched by 1-1.5 per mil. It remains uncertain if fractionation is influenced by H<sub>2</sub>O<sub>2</sub> concentration, temperature, or reaction time. Oxidation of pyrite by H<sub>2</sub>O<sub>2</sub> induces greater isotopic fractionation of sulfur than has been recognized in previous studies. Similar fractionation in nature could be mistaken as evidence for microbial activity.

